PYROLYTICALLY DERIVED REFRACTORY MATERIALS FOR AEROSPACE APPLICATION

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ABSTRACT

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The recent boom in rocket technology has had an equivalent reaction in the field of high temperature material research. Auxiliary propulsion systems for spacecraft are required to provide continuous or intermittent pulses for attitude control, orbital correction, rendezvous, etc. In the vacuum of space, radiation cooling is feasible.

Studies on free standing pyrolytic graphite indicated its potential applicability. As the investigation on pyrolytic graphite progressed, it became apparent that this material was the forerunner of a considerable family of pyrolytically derived materials, alloys, and mixed compounds. This paper reports comparative data on the thermal, mechanical, and physical properties of many such materials, gleaned from many sources. It presents experimental data on their oxidation rates in simulated combustion gases.

I INTRODUCTION

Materials with ordered structure derived by the thermal decomposition of gaseous compounds on a suitable, heated substrate are called pyrolytically derived or pyrolytic materials.

Historically, pyrolytic materials had their official beginning with the granting of a U. S. Patent to Thomas Edison in 1883, covering pyrolytic graphite as a material for electric lamp filaments. Severe limitations, on the sizes which could be made, forced exploration of other techniques and materials for filament use. For decades the idea of pyrolytically derived materials lay in obscurity. The Space Age, with its insatiable appetite for components with unique properties, reactivated interest in this special class of materials taking them once again to front stage center.

At first, prime interest turned to pyrolytic graphite. Techniques were developed to a point where solid bodies like re-entry heat shields and nose cones for hypersonic vehicles could be fabricated. These are several feet in dimensions and weigh several hundred pounds each. The natural desire to modify and improve properties, led to the introduction of various constituents into the pyrographite lattice. Boron, tungsten, zirconium, molybdenum, etc. modifications have been made with unique properties. Further exploratory development led to pyrolytic boron nitride and silicon carbide. Other metal carbides, mixed compounds and pure metals such as boron and tungsten followed on the heels of the aforementioned ones. The field of new pyrolytically derived materials is broadening constantly.

II PROCESS

The process by which pyrolytically derived materials are made, can be characterized as vapor plating. The pressure is controlled and the atmosphere in the chamber is that of the reactant gases. Sometimes an inert diluent gas is also employed. The reactant vapor, containing the metal or compound desired, decomposes upon approaching the heated substrate. The material nucleates on the heated surface, building up to the required section thickness. The deposits are ordered in crystallographic structure, exhibiting axial isotropy of thermal, physical, mechanical, and electrical properties according to their crystal habits. If desired, the substrate may be removed to leave a free standing structure. Materials, that can produce pyrolytic deposits, are limited to those compounds whose vaporization temperatures are below their decomposition temperatures and which separate cleanly from the vapors of their compounds.

Pyrolysed single compounds, such as boron chloride (BCl_3) deposits elemental materials such as Boron. Hydrocarbon gases yield carbon or graphite. Metallic halides yield the metals. Mixtures of reactants result in compound formation such as boron nitride, tungsten carbide, etc., and solid solutions or alloys such as pyrographite plus boron. The pyrolytically derived materials have high densities, approaching theoretical. They have closely controlled composition gained through the control of the reactant gases.

Pyrolytic deposition affords an intriguing technique for preparing dense bodies of refractory materials for aerospace application which

are not readily formed by other techniques. Table I lists materials melting above 4000°F. Those which are starred (*) have already been successfully deposited as pyrolytic materials. The remainder of the list are given for comparison and as subjects for further research as pyrolytic materials.

III PYROLYTIC MATERIAL'S PROPERTIES

Pyrolytically derived materials fall into two general classes; anisotropic and isotropic. Isotropic materials have uniform properties in all axial directions. Anisotropic materials have nonuniform properties in various axial directions.

A. Anisotropic Materials

Typical examples of anisotropic materials are graphite, and boron nitride. Their crystal structures are hexagonal. This results in preferred crystal orientation and produces substantial differences in properties such as thermal and electrical conductivity, mechanical strengths, and chemical reactivity between directions normal and parallel to the deposition surface. The degree of anisotropy can be controlled somewhat by control of deposition parameters. For pyrolytic graphite the ratio of difference in property values between the "c" and "a" axes may vary from 100 to 1 to 1000 to 1. This compares with commercial graphites with ratios of 3-4 to 1. For boron nitride, the ratio may be as high as 1900 to 1.

The wide difference in thermal conductivity values for pyrolytic graphite in the "a" and "c" directions are illustrated in Figure 1.

TABLE I

PROPERTIES OF SOME SOLIDS THAT MELT ABOVE 4000°F

Class	Solid	Chemical Formula	Melting Point (°F)	Boiling Point (°F)	Specific Gravity (Dense Form)
Pure Metals	Tungsten*	W	6170	10,600	19.3
	Rhenium*	Re	5755	8,700	20.0
	Tantalum*	Ta	5430	7,400	16.6
	Osmium	Os	4890	9,600	22.5
	Molybdenum*	Mo	4750	6,700	10.2
	Ruthenium	Ru	4530	4,900	12.2
	Iridium*	Ir	4445	8,700	22.5
	Columbium* (Niobium)	Cb (Nb)	4380	6,000	8.6
Oxides	Thoria	ThO_2	5970	7,950	9.7
	Magnesia	MgO	5070	5,115	3.6
	Hafnia	HfO_2	5020	--	9.7
	Zirconia	ZrO_2	4850	7,800	5.6
	Ceria	CeO_2	4710	--	7.1
	Calcia	CaO	4710	5,160	3.3
	Beryllia*	BeO	4620	7,700	3.01
	Strontia	SrO	4380	5,430	4.7
	Yttria	Y_2O_3	4370	7,800	4.9
	Lanthana	L_2O_3	4180	7,600	6.5
	Urania	UO_2	4140	7,450	11.0
	Chromia*	Cr_2O_3	4115	5,430	5.2
Complex Oxides	Thorium Zirconate	ThO_2ZrO_2	5070	--	--
	Strontium Zirconate	$SrOZrO_2$	4890	--	5.5
	Barium Zirconate	$BaOZrO_2$	4890	--	6.3
	Beryllium Zirconate	$3BeO_2ZrO_2$	4590	--	--
	Zirconium Silicate	ZrO_2SiO_2	4390	--	4.6
	Calcium Zirconate	$CaOZrO_2$	4240	--	4.8
Carbides	Hafnium Carbide*	HfC	7025	--	12.2
	Tantalum Carbide*	TaC	7015	--	14.5
	Zirconium Carbide*	ZrC	6890	9,200	6.7
	Columbium Carbide*	CbC (NbC)	6330	--	7.8
	Tantalum Carbide*	Ta_2C	6150	--	15.0
	Titanium Carbide*	TiC	5680	7,900	4.8
	Tungsten Carbide*	WC	5190	11,000	15.5
	Tungsten Carbide*	W_2C	5170	11,000	17.2
	Vanadium Carbide	VC	5730	7,050	5.4
	Aluminum Carbide	Al_4C_3	5070	--	3.0
	Molybdenum Carbide*	Mo_2C	4860	--	8.9
	Molybdenum Carbide	MoC	4870	--	8.5
	Thorium Carbide	ThC_2	4810	--	9.6
	Thorium Carbide	ThC	4760	9,050	10.6
	Boron Carbide*	B_4C	4440	--	2.5
	Silicon Carbide*	SiC	4350	--	3.2
	Uranium Carbide	UC_2	4260	7,900	11.3

(continued on next page)

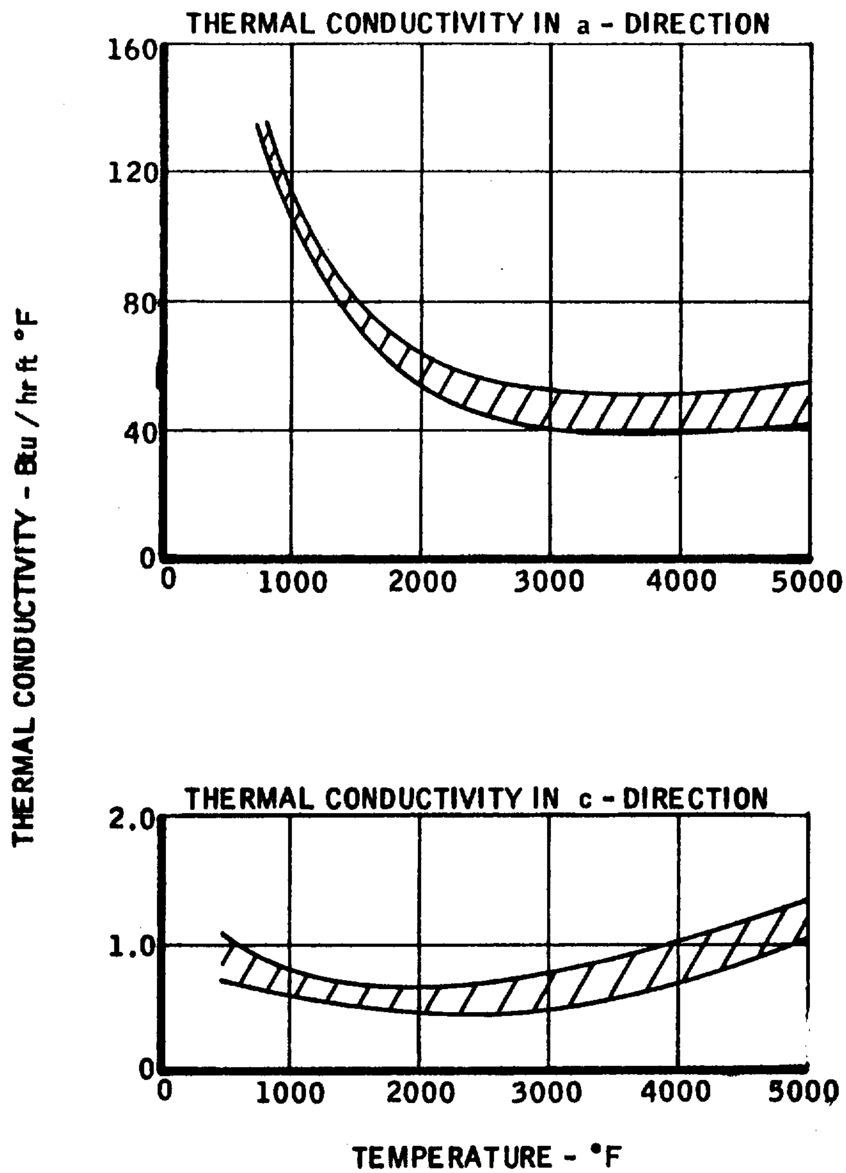
TABLE I (Continued)

Class	Solid	Chemical Formula	Melting Point (°F)	Boiling Point (°F)	Specific Gravity (Dense Form)
Borides	Chrome Nickel Boride	Cr_2NiB_4	4000	--	6.0
	Tantalum Boride	TaB_2	5440	--	12.60
	Niobium Boride	NbB_2	5250	--	7.21
	Chromium Boride	CrB_2	5000	--	5.6
	Tungsten Boride	W_2B	5020	--	16.7
	Hafnium Boride	HfB_2	5540	--	11.2
	Zirconium Boride	ZrB_2	5430	--	6.1
	Tungsten Boride	WB	5290	--	16.0
	Titanium Boride*	TiB_2	4710	--	4.5
	Thorium Boride	ThB_4	4530	--	8.45
Silicides	Tungsten Silicide	W_3Si_2	4250	--	--
	Tantalum Silicide	Ta_9Si_2	4550	--	12.7
	Tantalum Silicide	Ta_5Si_3	4530	--	11.6
	Zirconium Silicide	Zr_6Si_5	4080	--	--
Nitrides	Hafnium Nitride	HfN	5990	--	--
	Boron Nitride*	BN	5430	--	2.2
	Tantalum Nitride	TaN	5400	--	--
	Zirconium Nitride	ZrN	5390	--	6.9
	Titanium Nitride*	TiN	5340	--	5.4
	Scandium Nitride	ScN	4800	--	--
	Uranium Nitride	UN	4765	--	14.32
	Thorium Nitride	ThN	4280	--	--
	Aluminum Nitride	AlN	4050	--	--
Miscellaneous	Cerium Sulfide	CeS	4440	--	6.0
	Carbon, Graphite	C	6800	--	--
	Uranium Monocarbide	UC	4490	--	13.63
	Beryllium Nitride	Be_3N_2	4000	Dissoc.	--
Solid Solution Alloys	Graphite-Boron Alloy*				
	Graphite-Tungsten*				
	Graphite-Zirconium*				
	Graphite-Molybdenum*				
	Graphite-Titanium				

* Successfully deposited as pyrolytic materials.

THERMAL CONDUCTIVITY OF PYROLYTIC GRAPHITE

REFERENCE: HIGH TEMPERATURE THERMAL PROPERTY MEASUREMENT TO 5000°F, BY NEEL & PEARS, JAN. 1962



The anisotropy in mean coefficients of thermal expansion for pyrographite and for boronpyralloy (Pyrographite plus Boron) are compared with several high temperature metal alloys in Figure 2.

B. Typical Applications for Anisotropic Materials

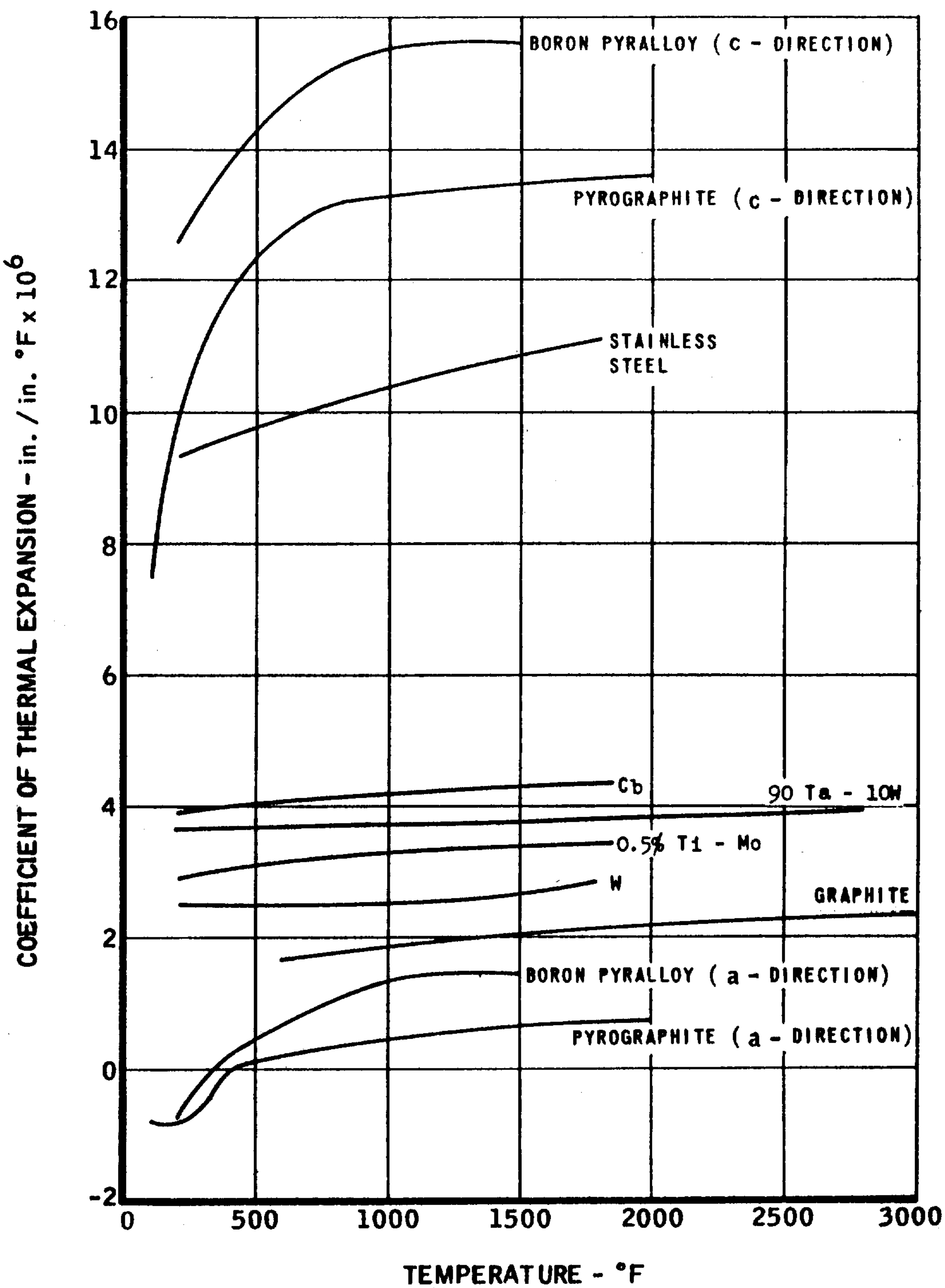
Anisotropic materials are exploited for their marked property differences along different axial directions. Heat or electrical energy can be directed in preferred orientation to attain unique results achievable with no other single materials. Such materials can simultaneously be insulators and conductors according to axial utilization. These remarkable materials are currently being tested for use as small free standing, light-weight, radiatively cooled rocket chambers.

Illustrations of thrust chambers constructed of anisotropic materials are depicted in Figures 3, 4, and 5 entitled respectively, "Pyrolytic Graphite Composite Thrust Chambers," "Pyrolytic Boron-Nitride Thrust Chambers," and "Boron-Pyralloy Thrust Chamber Assembly."

C. Isotropic Materials

Typical examples of isotropic pyrolytically derived materials are the carbides of columbium, tantalum, and hafnium which form face centered cubic crystals and metallic tungsten which forms body-centered cubic crystals. Being isotropic, these materials have uniform properties in various directions from the substrate surface upon which they have been deposited.

MEAN COEFFICIENTS OF THERMAL EXPANSION FOR SELECTED NOZZLE MATERIALS
(FROM ROOM TEMPERATURE)



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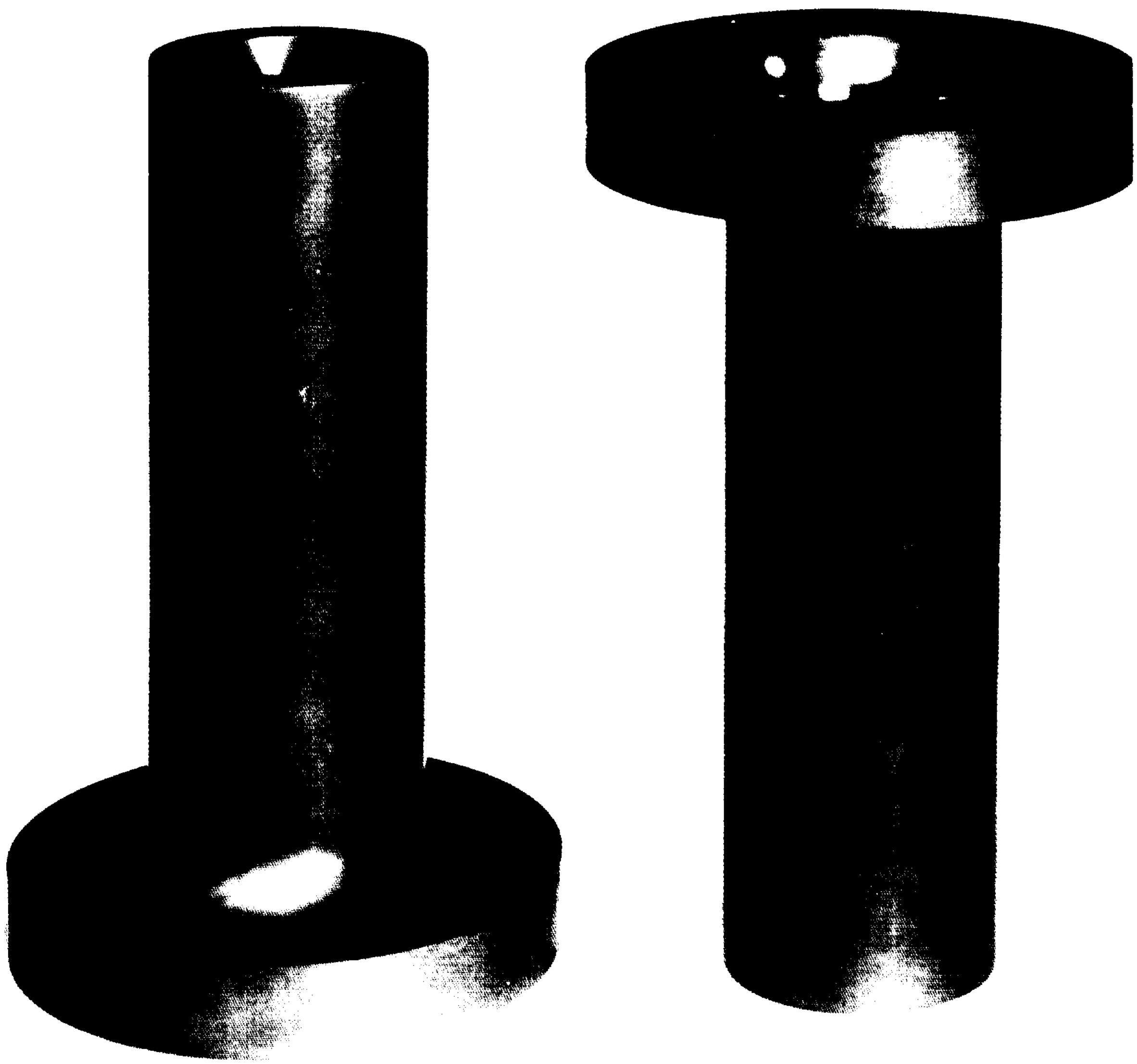
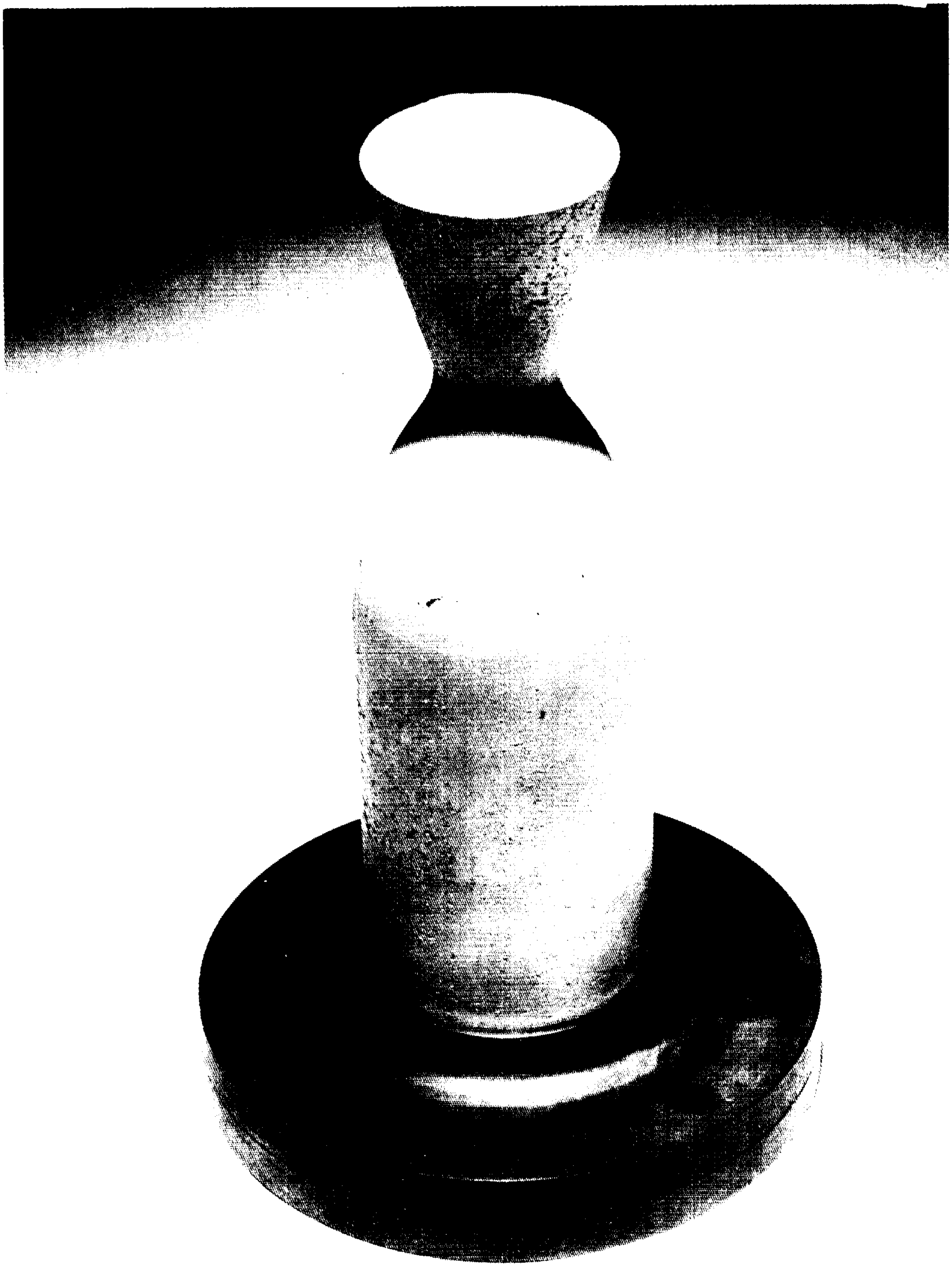


PYROLYTIC GRAPHITE COMPOSITE THRUST CHAMBERS

Figure 3



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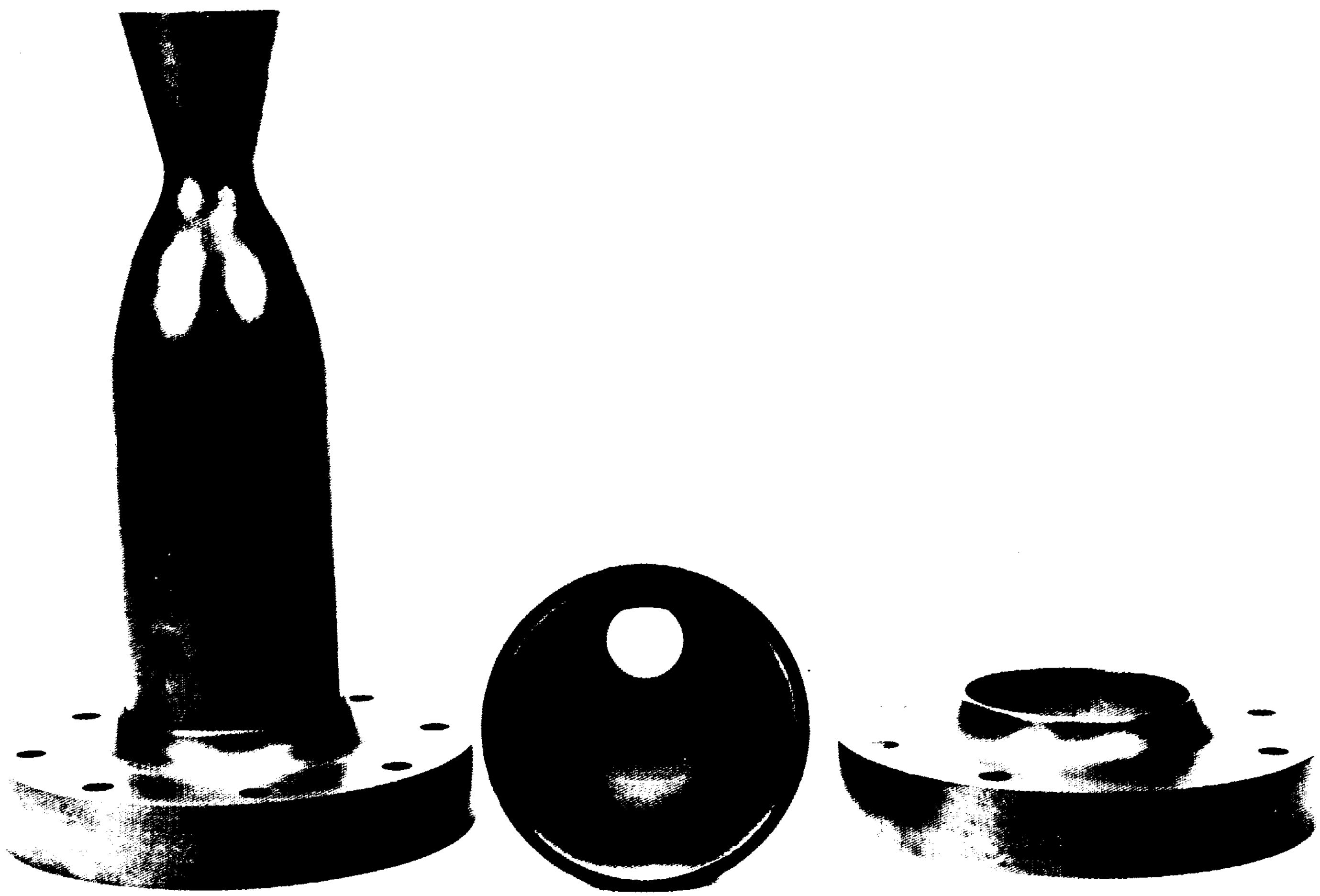
PYROLYTIC BORON NITRIDE THRUST CHAMBER

Figure 4



PYROLYTIC GRAPHITE COMPOSITE THRUST CHAMBERS

Figure 5

The pyrolytic deposition process is controllable so that carbides of varying metal-carbon ratios may be derived. Such variance in composition is reflected in their microhardnesses, which increase with increasing carbon content. Knoop hardness number ranges (K_{100}) for three groups of carbides follows

$Ta\ C_x - TaC_y$	-	1400-3500
$HfC_m - HfC_n$	-	2000-3600
$CbC_a - CbC_b$	-	1700-4000

where $y > x$, $N > M$, $b > a$.

Increasing hardness is accompanied by decreasing ductility and strength. Except for the high hardness grades, bend strengths lie in the 10,000 - 40,000 psi range. However, a value as high as 150,000 psi has been reported for TaC.

Pyrolytic tungsten exhibits Knoop hardness values from 415 to 1099 varying directly with decreasing grain size. Also increasing purity appears to increase hardness.

D. Typical Applications for Isotropic Materials

Pyrolytic tungsten is finding increasing use in the form of sound coatings such as large nozzles for rockets and missiles as well as for free standing shapes not readily produced by more conventional fabrication techniques.

The pyrolytic carbides have been utilized primarily as a protective hard facing on graphite or pyrographite substrates. As such, they

have performed very satisfactorily and have resisted the combustion products of aluminized solid propellants and liquid UDMH-N_2O_4 with negligible erosion. Flame temperatures varied from 5200 - 5800°F. The data for tests of these materials are given in Table II. Comparative data for similar propellants, (flame temperatures ranged between 3000 - 7000°F including tests in the 5200 - 5800°F range), show a considerably greater erosion rate for pyrographite and 1% Boron-PG than for the carbide coated materials. These data are given in Table III. Although the testing of pyrolytic tungsten has been limited in number and scope, the results as shown in Table IV, indicate a marked resistance to erosion at 6200°F to the combustion products of aluminized solid propellant.

E. Property Data and Discussion

Comparative chemical stabilities to propellants of those pyrolytic materials tested to date are also presented in a series of tables as follows:

Table II - Chemical Stability to Propellants of Pyrolytic Carbides

Table III - Chemical Stability to Propellants of Pyrographite and 1% Boron in Pyrographite

Table IV - Chemical Stability to Propellants of Pyrolytic Tungsten

TABLE II

CHEMICAL STABILITY TO PROPELLANTS OF PYROLYTIC CARBIDES

Nozzle Configuration	Propellant	No. of Times Fired	Throat Diameter (inches)	Nominal Pressure (psi)	Flame Temperature (°F)	Total Firing Time (seconds)	Throat Erosion Rate (mils/sec)
HfC 0.005" coating on graphite	Solid (Aluminized)	1	0.5	440	5600	71	Negligible
CbC 0.005" coating on graphite	Solid (Aluminized)	1	0.6	800	5600	30	Negligible
CbC 0.010" coating on graphite	Solid (Aluminized)	1	0.6	640	5600	42	Negligible
CbC 8-10 mils on graphite	Liquid $UDMH-N_2O_4$	1	1.5	150	5200	120	Negligible
SiC	Liquid	1	--	800	5500 - 5800	120	Negligible
TaC 0.020" coating on graphite	Solid (Aluminized)	1	0.6	750	5600	65	Negligible
TaC 5-8 mil coating on graphite	Liquid $UDMH-N_2O_4$	2	1.5	150	5200	180(a)	Negligible
TaC 8-10 mil coating on graphite	Liquid $UDMH-N_2O_4$	3	1.5	150	5200	300(b)	0.003
TaC 3-5 mil coating on graphite	Liquid $UDMH-N_2O_4$	1	1.5	150	5200	90	0.003
ZrC 7.5 mil coating on graphite	Liquid $UDMH-N_2O_4$	2	1.5	150	5200	165(c)	Negligible

(a) 120 seconds, then 60 seconds.

(b) 120 seconds, 120 seconds, then 60 seconds.

(c) Fired 125 seconds and 40 seconds.

TABLE III

CHEMICAL STABILITY TO PROPELLANTS
PYROGRAPHITE AND 1% BORON IN PYROGRAPHITE

Nozzle Configuration	Propellant	No. of Times Fired	Throat Diameter (inches)	Nominal Pressure (psi)	Flame Temperature (°F)	Total Firing Time (seconds)	Throat Erosion Rate (mils/sec)
Washer Nozzle Graphite Sleeve (Heat Sink)	Solid (Aluminized)	1	0.5	750	6600	70.0	0.30
Washer Nozzle Graphite Sleeve (Heat Sink)	Solid (Aluminized)	1	0.5	700	5900	7.2	0.05
Washer Nozzle Graphite Sleeve (Heat Sink)	Solid (Aluminized)	1	0.2	--	3000	30.0	--
Washer Nozzle Graphite Sleeve (Heat Sink)	Solid (Aluminized)	1	4.5	300	6700	65.0	0.25
Washer Nozzle Graphite Sleeve (Heat Sink)	UDMH-N_2O_4	2	0.5	400	5200	125.0	--
Washer Nozzle Graphite Sleeve (Heat Sink)	$H_2 + O_2$	1	1.25	125	5120	35.0	0.5
Washer Nozzle Graphite Sleeve (Heat Sink)	$H_2 + F_2$	2	0.75	300	7000	150.0	0.15
Free Standing with Graphite Backing Insulation	Solid (Aluminized)	1	0.70	700	6400	40.0	0.26
Free Standing with Graphite Backing Insulation	Solid (Aluminized)	1	0.65	1100	6400	30.0	0.55
Free Standing (Insulating) no back-up	N_2O_4 - N_2H_2	2	0.80	125	5000	80.0	0.3
Erosion Results of 33 Firings	Solid (Aluminized) 15-22%	-	0.5-3.8	280-1200	5500-6300	38.0-72.0	0.14-0.40
			PG + 1% BORON				
Free Standing with Graphite Backing-Insulation	Solid (Aluminized)	1	0.5	525	6200	56.0	0.48
Free Standing	Liquid N_2O_4 - N_2H_2 / Solid (Aluminized)	4	0.80	100	5000	120.0	0.25

TABLE IV

CHEMICAL STABILITY TO PROPELLANTS
OF PYROLYTIC TUNGSTEN

Nozzle Configuration	Propellant	No. of Times Fired	Throat Diameter (inches)	Nominal Pressure (inches)	Flame Temperature (°F)	Total Firing Time (seconds)	Throat Erosion Rate (mils/sec)
0.074" Thick Coating on Graphite	Solid (Aluminized)	1	4.5	320	6200	70.0	--

Comparative thermal, physical, and mechanical data are presented in a series of tables as follows:

Table V - Pyrographite, 1% Boron in Pyrographite, and Boron Nitride

Table VI - Pyrolytic Carbides

Table VII - Pyrolytic Titanium Nitride, Titanium Boride, and Tungsten

In Table V it is interesting to note that the addition of 1% Boron into the PG lattice has decreased the thermal conductivity of PG 74% in the "a" direction and increased it 102% of PG in the "c" direction, thus increasing the total anisotropy of the resulting product. Comparing PG and BN we find that both materials expand equally on the "a" axis and that BN expands 167% greater than PG on the "c" axis; BN is the better thermal insulator. Its thermal conductivity in the "a" axis is only 16.9% of PG, while in the "c" direction its thermal conductivity is 82% of PG. Other properties are similarly affected.

In Table VI, as we proceed from stoichiometric to carbon rich compositions, the resulting products increase markedly in harness, a seeming anomoly. It is also interesting to note that the room temperature bend strengths are in the same range with the exceptions that metal rich TaC has been measured at 150,000 psi and Zr rich at 90,000 psi.

TABLE V

PYROLYTIC MATERIAL

PYROGRAPHITE, 1% BORON
IN PYROGRAPHITE AND BORON NITRIDE

PROPERTY	BN	PG	PG + 1% BORON
Melting Point	--	--	--
Sublimation Temperature (°F)	5430	6600	6600
Coefficient of Thermal Expansion			
"a" direction (°C)	1×10^{-6}	1×10^{-6}	--
(°F)	1.8×10^{-6}	1.8×10^{-6}	--
"c" direction (°C)	25×10^{-6}	27×10^{-6}	--
(°F)	45×10^{-6}	15×10^{-6}	--
Density gm/cm^3	2.1 - 2.2	2.26	2.19 - 2.22
lbs/in^3	.076 - .079	.079	.079
Thermal Conductivity			
"a" direction			
$cal/cm^2/sec/°C/cm$			
100°C (212°F)	0.15	--	--
$Btu/hr/Ft^2/°F/in.$			
70°F	--	2580	1920
212°F	435	--	--
400°F	--	3000	--
500°F	--	2460	--
1000°F	--	2040	--
1500°F	--	1560	--
3000°F	--	500	--
"c" direction			
$cal/cm^2/sec/°C/cm$			
100°C (212°F)	0.004	--	--
$Btu/hr/ft^2/°F/in.$			
70°F	--	12.96	13.2
212°F	10.6	--	--
500°F	--	10.68 - 11.00	--
1000°F	--	8.75 - 9.6	--
1500°F	--	8.52	--
2000°F	--	9.6	--
3000°F	--	10.2	--
Specific Heat			
Btu/lb/°F			
R.T.	0.24	--	--
500°F	--	0.30	--
1000°F	--	0.38	--
1500°F	--	0.45	--
2000°F	--	0.51	--

(continued)

TABLE V (Continued)

PROPERTY	BN	PG	PG + 1% BORON
Emittance			
Spectral (1000 - 1500°C) (1872 - 2732°F)	0.6 - 0.8	--	--
30° to "a" - 3000°F	--	0.6	--
"c" direction			
1000°F	--	0.77	--
1500°F	--	0.5 - 0.8	--
2000°F	--	0.83	--
3000°F	--	0.9	--
3500°F	--	0.8 - 0.9	--
Flexural Ultimate (Modulus of Rupture)			
Bend Strength (psi) "a" direction	15,000 - 27,000	--	16,000 - 30,000
Perpendicular to "c"			
70°F	--	25,000	--
3632°F	--	35,500	--
Parallel to "c"			
70°F	--	23,500	--
3632°F	--	32,000	--
Tensile Strength (psi)			
"a" direction			
70°F	--	14,000 - 40,000	16,500
3000°F	--	16,000 - 50,000	--
4000°F	--	33,600	--
5000°F	--	41,000	--
"c" direction			
70°F	--	732 - 1,500	649
3000°F	--	213	--
4000°F	--	240	--
Elastic Modulus (psi x 10^6)			
"a" direction	3.0 - 4.4	--	4.61 in tension
"c" direction	--	1.50	--
Parallel to basal plane	--	4.38	--
Perpendicular to basal plane	--	4.39*	--

*NOTE: 13 x 10^6 is highest actual modulus achieved.

(continued)

TABLE V (Continued)

PROPERTY	BN	PG	PG + 1% BORON
Creep Properties	--	Tensile: Stress level ~ 20% of UTS. At R.T., no creep after 260 hours.	Very little at 30,000 psi and 4500°F
Poisson's Ratio			
"a" direction	-0.025	--	--
Loaded in tenion in "a" direction	--	--	-0.176
Parallel to basal plane	--	0.9 to 0.94	--
Perpendicular to basal plane	--	0.2 to 0.34	--
"c" direction	--	-0.12 to -0.18	--
Hardness (Knoop)			
Kg/mm^2 on edge	--	27 - 28	430
on planes	--	84 - 91	--
Oxidation Resistance (slow moving air)			
1000°F "ab" direction	--	0.015 $mg/cm^2/min.$	--
"c" direction	--	0.0375 $mg/cm^2/min$	--
1292°F	--	--	--
2372°F in/hr.	< 0.001	--	--
Micro-Structure			
Crystal Habit	Hexagonal	Hexagonal	Hexagonal
Crystal layer spacing	3.36Å	--	3.42Å
Crystal size	50 - 100Å	--	100Å
"a" direction	--	6.68Å	--
"c" direction	--	6.818 - 6.847Å	

TABLE VI

PYROLYTIC CARBIDES

Property	HFC	NbC	SiC	TaC	ZrC	20% Zr in PG
Melting Point - °F Sublimation Temperature - °F	7030 --	6330 --	-- 4892 (Dissociates)	7020 --	6332 --	-- --
Coefficient of Thermal Expansion (70 - 2192°F) 1×10^{-6}/°F	12.4	--	7.2 8.1 "ab" direction	--	11.5	5.4
Density - gm/cm^3 lbs/in^3	12.2--12.7 0.44--0.46	7.8--7.97 0.28--0.29	8.9 0.32	14.1 0.51	6.0 0.22	-- --
Thermal Conductivity Btu/hr/ft^2/°F/in.	--	93.8	116.0	154.0	319.0	--
Emittance - 3272°F 4892°F	-- --	-- --	-- --	0.36 0.44	-- --	-- --
Flexural Ultimate (Modulus of Rupture) Bend Strength - psi	10,000 - 40,000	10,000 - 40,000	33,000	10,000 - 40,000*	10,000	90,000
Tensile Strength - psi	--	--	60,000	3,000	--	--
Elastic Modulus - 1×10^6 psi	--	--	--	4.15	--	--
Hardness (Knoop) - (Kg/mm^2) Stoichiometric Carbon Rich	1960--2400 4000	2700 3500	2600 --	2100--2400 2400--3500	2356 --	-- --

(*NOTE: Metal rich TaC went as high as 150,000 psi)

(Continued)

TABLE VI (Continued)

Property	HFC	NbC	SiC	TaC	ZrC	20% Zr in PG
Oxidation Resistance						
$gm/cm^2/hr$						
900°C (1652°F)	--	--	0.0128	0.0396	starts at 700°C	--
1000°C (1832°F)	0.01	--	0.0236	0.1673		--
1200°C (2192°F)	--	--	0.0620	0.5830		--
1400°C (2552°F)	--	--	0.0908	2.0840		--
			To 1600°C*			
Micro-Structure						
Crystal Orientation	70:1	3000:1	--	--	--	--
Lattice Constant	4.63Å	4.46Å		4.43Å	--	--
	FCC Metallic	FCC Metallic	Depending on carbon content) FCC Metallic to Graphite	FCC Metallic	--	Graphitic

* To 1600°C, as a 3-4 mil thick coating on graphite, only a slight increase in weight (XS free Si) after 12,000 - 13,000 hours at 1830°F in slow moving air. Durability - 40 days at 2300°F and few days at 2500°F.

TABLE VII

PYROLYTIC W, TiN, TiB_2

Property	TiN	TiB_2	W
Melting Point	2950°C at 1 Atm N_2	--	3410°C (6170°F)
Coefficient of Thermal Expansion in/in/°F - "ab" direction	--	--	7.9×10^{-6}
Density - gms/cc lbs/in^3	5.4 - 5.56 .17 - .20	-- --	19.3 .695
Thermal Conductivity in "a" direction Btu/hr/ft^2/°F	--	--	8.20 - 11.40
Flexural Ultimate (Modulus of Rupture) psi	--	51,000	--
Elastic Modulus - psi	8060	--	--
Hardness (Knoop) (increasing in decreasing grain size)	2350	--	415 - 1090
Micro-Structure	--	--	BCC

IV TRENDS AND EXPECTATIONS FOR PYROLYTIC MATERIALS

As development of pyrolytic materials proceeds, materials of increased strength, hardness, and oxidation resistance will be discovered. Many of these newer materials will be isotropic, however, further developments in anisotropic materials can be anticipated. Advantage will be taken of outstanding oriented properties to develop unique componants.

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APPENDIX A

BIBLIOGRAPHY OF DATA SOURCES

1. Arthur D. Little, "Development of Pyrolytic Materials for Solid Fuel Rocket Motor Applications," - R. Francis - Contract NO DA-19-020-ORD-5490; 10 October 1961.

2. High Temperature Materials, Inc., - Data Sheet - "PG (Pyrolytic Graphite)" - 6 October 1961, Revised 12 February 1963.

3. Nerglho, Inc., - Data supplied by H. A. Ohlgren.

4. American Metal Products Company, - Data supplied by Dr. K. S. Sanvordenker.

5. General Electric Company, - "Pyrolytic Graphite - Preliminary Engineering Data."

6. High Temperature Materials, Inc. - Data Sheet - "Pyrolytic Carbides," 1 October 1962.

7. High Temperature Materials, Inc. - Applications Data -"Pyrolytic Materials," - 1 October 1962.

8. Raytheon Company - "Pyrographite"

9. Southern Research Institute, - "Summary Report 6216-1209-XVII, November 24, 1961 to Lockheed Missiles & Space Company - "Some Thermophysical Properties of Pyrolytic-Graphite to 5200°F."

10. Pappis, J. and Blum, S. L. - "Properties of Pyrolytic Graphite," - Journal of the American Ceramic Society, Vol. 44, No. 12, pp 592-597 - December 1961.

APPENDIX A (Continued)

11. Bourdeau, Dr. R. G., - "New Pyrolytic Materials," - Materials in Design Engineering - August 1962, pp 106-109.

12. Cacciotti, J. J. - "Pyrolytic Graphite Development," - Paper presented to the Fourth Refractory Composites Working Group, 15-17 November 1960.

13. Yaffee, M. - "Pyrolytic Graphite Studied for Re-Entry" - Aviation Week and Space Technology - 25 July 1960, Reprint.

14. Yaffee, M. - "Pyrolytic Graphite Gains as Heat Shield" - Aviation Week and Space Technology - 13 February 1961, Reprint.

15. Jet Propulsion Laboratory, T.R. No. 32-71 - "Tensile Properties of Pyrolytic Graphite to 5000°F" - Contract No. NASW-6.

16. National Carbon Company, Research Laboratory - WADD T.R. 61-72, Vol. I - "Research and Development on Advanced Graphite Materials" - September 1961.

17. General Electric Company, Final Report on LMSD Statement 83 - "Improvement of Pyrolytic Graphite Properties by Heat Treatment and Hot Working - Initial Evaluation of Structure and Properties" - December 1961.

18. The Beryllium Corporation Brochure - "Pyrolytic Graphite."

19. High Temperature Materials, Inc., Data Sheet - "Pyrolytic Tungsten" - 9 May 1962.

APPENDIX A (Continued)

20. High Temperature Materials, Inc., Data Sheet - "Boron Pyralloy" 6 November 1961.

21. High Temperature Materials, Inc., Data Sheet - "Boralloy" - 1 September 1962.

22. Levy, M. - "Oxidation of Pyrolytic Graphite in Air Between 1250° and 1850°F" - I. & E. C. Product Research and Development, Vol. 1, pp 19-23 - March 1962.

23. Klein, C. A. - "Electrical Properties of Pyrolytic Graphites" - Reviews of Modern Physics, Vol. 34, No. 1, pp 56-79 - January 1962.

24. Riley, M. W. - "The New World of Carbon and Graphite" - Materials in Design Engineering, Manual No. 199, pp 113-128 - September 1962.

25. Raytheon Company, T.R. No. R-61 - "Pyrographites, Pyrographalloys, and Pyrofibers" - 23 March 1962.

26. Raytheon Company, T.R. No. R-63 - "Pyrolytic Graphite, An Initial Assessment" - 3 July 1962.

27. The Marquardt Corporation, Report 5907 - "Pyrolytic Graphite Rocket Thrust Chamber Development" - Contract NAS 7-54 - 31 July 1962.